ENERGY DISPERSIVE K X-RAY FLUORESCENCE ANALYSIS FOR ON-LINE PROCESS CONTROL OF HEAVY METAL CONCENTRATIONS

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INTRODUCTION

X-ray analysis has traditionally been wavelength dispersive, manpower intensive, and an analytical laboratory tool employing massive and costly x-ray generators and diffraction spectrometers. Following the development of the lithium drifted silicon and germanium [Si(Li) and Ge(Li)] semiconductor radiation detectors in the mid 1960's, and more recently the high purity germanium detector [HPGe], the analytical technique of energy dispersive x-ray fluorescence analysis (XRFA)[1] matured during the 1970's.

Essentially, energy dispersive x-ray fluorescence analysis (XRFA) is possible because each element has one or more unique and well known series of x rays. The K-series of x rays are more energetic than the L-series, which are in turn more energetic than the M-series, etc. By using an appropriate exciting radiation any atom can be stimulated to emit its x rays. The intensity of emitted x rays can be related to the concentration of elements present through appropriate calibration equations. Thus, a suitable x-ray detector coupled to a computer-based analyzer forms an x-ray spectrometry system. This system can be used to measure the intensity of emitted x rays, hence elemental concentrations.

By using selected radioactive sources it is now possible to measure nondestructively quantitative concentrations of heavy metals from process streams directly through industrial-gauge pipes. The concentrations can be obtained on-line and in near-real-time to control the chemical process, or coupled with flow rates, can give a quantitative evaluation of total inventory contained in product storage tanks.

MEASUREMENT SYSTEM DESCRIPTION

In order to perform quantitative x-ray fluorescence analysis several different components are required. A semiconductor detector or more specifically a high purity germanium detector (HPGe) housed in a sealed, evacuated cryostat is required to measure the stimulated x-ray emission. This HPGe detector must be operated at liquid nitrogen (LN) temperature (77°K).

To stimulate x-ray emission no x-ray tube is required. Instead, one or usually two 5 to 10 millicurie radioactive Co-57 sources are used. These sources are mounted in a custom-machined source holder that also serves to collimate the x rays emitted from the sample into the HPGe detector. The 122-keV photons from the Co-57 sources easily penetrate stainless steel or copper pipes to excite the K x rays of heavy metals ($Z \geq 72$), which in turn, also penetrate the pipes to be detected by the HPGe detector. Thus, no special constraints on process solutions are required. Furthermore, the exciting sources and detector collimation assembly measures only 3.0 inches in diameter by 2.0 inches thick, and with the HPGe detector, can be located remotely from the controlling computer-based operations console.[2]

Analog electronics (detector preamplifier and amplifier) are used to shape and process electronic pulses from the HPGe detector. An analog to digital converter (ADC) changes the analog pulses to digital bits which are sorted and stored in a multichannel analyzer. In effect, the x-ray energy detected and processed determines the pulse height distribution displayed by the multichannel analyzer.

A minicomputer is used to select and integrate those x-ray peaks of interest, then it converts integrated areas into concentration via appropriate calibration equations. A video terminal and/or printer displays/prints concentration results.

RESULTS

Concentrations from 0.5g/l to 500g/l can be derived from calibration data that ratio the net Kα1 x-ray peak area intensity to the incoherently scattered exciting radiation. Results accurate to better than 5% are acquired (thus reportable) periodically with the time interval being dependent on concentrations. If desired, accuracy can be improved to better than 1% by careful calibration, appropriate increases in measurement times, and measurement of the intensity of a third, highly collimated Co-57 source that transmits a beam through the entire pipe.[3] Ratioing net Kα1 x-ray intensity to transmitted 122-keV intensity allows concentrations to be determined independent of minor changes in the matrix composition

(density) of the process solution. In both the 2-source and 3-source approach, the ratio measured is independent of source half-life (270d). The sources normally require changing only once a year.

As mentioned above quantitative analysis times depend on several factors. The more important factors include desired accuracy, concentration, and atomic number. The closer the K-binding energy is to the exciting radiation energy (122.05 keV in this case), the better the excitation efficiency. Hence, plutonium (Z=94) with K_b = 121.7 keV and uranium (Z=92) with K = 115.6 keV are stimulated most effectively by the 122.05 keV exciting radiation. Metals such as tungsten (Z=74), gold (Z=79), or lead (Z=82) have K-binding energies between 69 and 88 keV, hence are fluoresced somewhat less effectively. The fluorescence efficiency is about a factor of three less for Hf (Z=72) than for Pu (Z=94).

Concentration will also govern the excitation time required to achieve a desired accuracy. The greater the concentration the less time required to achieve a desired measurement accuracy. If the concentration is fixed and greater measurement accuracy is desired, more time is required to accumulate experimental data (statistics). As an example a 1% statistical accuracy can be acheived in 210 seconds for a solution containing 10 grams of platinum per liter. If 3% accuracy were sufficient, then only 20 seconds of analysis time would be required. If the concentration were only one gram of platinum per liter and 10% accuracy were sufficient, then about one minute of analysis time would be required. Increased accuracy scales as the square root of the time, while changes in concentration scale linearly for a given precision. For hafnium (Z=72) at 10g/l, 300 seconds is required for 1% accuracy, for gold (Z=79) 200 seconds is required, and for plutonium (Z=94) 100 seconds is required - each at 10g/l and 1% measurement accuracy. These times apply for solutions flowing (or static) through 1.0 to 2.0-inch diameter pipes.

The first K XRFA system was installed at the Savannah River reprocessing plant facility in 1981.[3] It was designed to allow measurement of pure plutonium (Pu), and occasionally mixed uranium + plutonium (U+Pu) solution concentrations brought to an off-line measurement station from any one of 34 different process inspection points or storage tanks. This system employs the 3-source approach because of the need for high accuracy.

At the Allied General Nuclear Services plant, three K XRFA systems were installed in 1981 to provide quantitative determinations, on-line and in near-real-time, of U stream concentrations for process control.[4] All systems use the 2-source approach. Additional systems are now being designed to monitor on-line Pu concentrations using both 2- and 3-source approaches.

At the Idaho Chemical Processing Plant a 2-source system is being installed on-line to monitor U-235 concentrations in an organic reprocessing stream.

CONCLUSIONS

Presently, a complete K x-ray fluorescence analysis system costs about $45,000. Major component costs break down as follows: HPGe Detector $8500; two radiation sources, $1500; customized machined source/detector assembly $2500 or more; analog electronics $6500; a multichannel analyzer $15,000 or more; a minicomputer $10,000 or more; and a printer $1000 or more. All but the customized machined component can be purchased from various commercial vendors.

There are some improvements that can be expected in the future. Among these will be a reduction in the size, amount, and sophistication of support electronics. The minicomputer can be replaced by a microprocessor, particularly for industrial process-stream monitoring applications in which the same element is repetitively analyzed. In this case, it is likely that most, if not all, of the electronics will fit into a single nuclear instrument bin. Also, if a sufficient industrial demand for such K-XRFA systems arises, they may become commercially available. If this occurs, the price might decrease to between $20,000 to $25,000 for the entire system. So far, each system assembled has been designed around specific requirements for either uranium or plutonium concentration measurements.

In summary, the K x-ray fluorescence analysis technique is innovative and practical for on-line or off-line, near-real-time applications because:

- It offers a compact x-ray fluorescence design, i.e., no x-ray tube is required.
- It allows the exciter-detector assembly to operate remotely from support electronics.
- It can be configured to operate either on-line or off-line for monitoring or measuring.
- The system can be run by semi-skilled, but trained technicians once programmed.
- It can be operated by remote TTY terminal and send results to plant control rooms.
- It measures pure heavy metals ($Z \geq 72$), or mixed metal/stream concentrations nondestructively through pipes.

- It can measure these concentrations independent of minor solution matrix changes.
- It reports concentration results in near-real-time.
- Measurement times of $\leq$20 s to $\leq$50 m give 1% accuracy for metal concentrations of 200 g/l to 1 g/l (for Z $\geq$ 72).
- The dynamic range of concentrations measureable is over 10^3 (from less than 0.5 g/l to 500 g/l).
- It meets the $\leq$0.5% accuracy required by DOE for nuclear materials safeguards accountability of U and/or Pu once a system has been calibrated carefully.

For more detailed information the interested reader is encouraged to contact the author directly.

REFERENCES

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